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BRIGHTENING ALUMINUM AND ALUMINUM ALLOY SURFACES

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The present invention consists in the production of brilliant reflecting surfaces on aluminum or aluminum alloys, that is to say a treatment of the said surfaces for improving the reflective power thereof. The aluminum may be in the form of sheets or the like, or made into the form of various articles of commerce.

More particularly the invention has for its object a process permitting the obtainment on an aluminum surface or on the surface of any one of a great number of aluminum alloys, a surface which is highly reflective to light rays and heat rays, this being possible even in articles of complicated construction. The process makes unnecessary a previous mechanical or other polishing or grinding of the surface of the article.

It is known that the surfaces of pure aluminum and of aluminum alloys, treated electrolytically in certain solutions and under very precise conditions can acquire particularly reflective surfaces for light rays and heat rays. This operation has generally been called by the name "brightening." Heretofore the brightening of the surface has usually been accomplished by an anodic oxidation treatment, there being produced a thin transparent and brilliant film of hydroxide of aluminum, formed during the process, giving the articles a more or less durable reflecting power. But the reflecting character or the surface, in articles produced according to the known processes, may be lost by tarnishing under the action of atmospheric moisture.

Numerous solutions have been proposed, and some of these have been patented, for use in the prior art processes. These include fluoboric acid, sulpho-phosphoric acid, phosphate and carbonate of soda, etc. It has been known for a long time that solutions of tri-sodium phosphate, preferably hot, leave on the surface of the aluminum a somewhat "satin-like" and brilliant aspect. These solutions have to be used by chemical or electrolytic methods. Always however, the reflective power of the surfaces so obtained is insufficient for making a good reflector.

The utilization as electrolytes of solutions of a mixture of phosphate and carbonate of soda, heated at 85° C., the aluminum article constituting the anode, permits of obtaining fairly good reflecting surfaces on articles of pure aluminum if the aluminum is sufficiently refined, and such a process is now in commercial use.

The principal inconveniences of the above mentioned methods are:

(*a*) It gives sufficiently satisfactory results, from the point of view of durability, only on highly refined aluminum, which is very costly,

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(*b*) It is necessary to store the solutions, for a longer or shorter time, to allow the same to age. In other words, the freshly obtained solution used in treating the surface, gives a less brilliant surface than when using a solution which has already been used for a substantial period.

(*c*) The thin film of aluminum hydroxide which is transparent, obtained in the process of producing brilliant surfaces, is pulverulent, and to some extent shows somewhat dust-like through the oxide formed in the anodic oxidation, and then, even after a sealing in boiling water, has to be revived or restored, by polishing the pieces after the process has been completed, in order to make it possible to touch the pieces with the fingers, without leaving finger-marks.

(*d*) The "penetrating" of the current through the solutions is not very good, that is to say, the electrostatic field lines do not pass throughout the whole solution, so the recessed parts of an aluminum object placed in such solutions cannot be satisfactorily brightened unless an auxiliary cathode is introduced inside said recessed portions of the said object.

(*e*) The anodic oxidation following the electrolytic brightening, as carried out with sulphuric acid solutions often leaves some portions of the surface dull and not sufficiently brightened even though a casual or brief glance might give the impression of a well brightened surface. These pieces which have portions of the area dull have to be treated for the removal of the coating by special solutions, and then can again be subjected to the brightening process.

The present invention permits the avoidance of these inconveniences. The process gives a brilliant and reflective surface on objects of aluminum or aluminum alloys, by the following steps. After being well degreased, the article is immersed in a phospho-chromic acid solution which is strongly acid, then it is submitted to an anodic electrolytic treatment in an alkaline bath containing principally the ions PO_4^{---} and AlO_2^-. The article is again immersed in a phospho-chromic acid solution, and is finally submitted to an anodic oxidation in an acid solution (which solution may be itself old in this art). The article can be then colored or sealed if desired.

For the successful carrying out of the process according to the invention, the said operations can be conducted in the following manner.

1. The degreasing is preferably carried out electrolytically, according to any known method,

in any convenient solution, for example a mixture of carbonate, phosphate and silicate of soda. The article, in this operation, constitutes the anode. At a tension of 8 to 12 volts, and at approximately room temperature, a treatment for one minute is usually sufficient. The article is then rinsed, preferably in running water.

2. The article is immersed in a strongly acid solution composed of phosphoric acid, chromic acid and water. In this solution the phosphoric acid dominates over the chromic acid. This solution preferably contains about 30% to 35% of phosphoric acid and about 10% to about 15% of chromic acid, both by weight. The pH of the solution is in general below 1 and preferably below 0. It is somewhat difficult to accurately measure the pH of such a solution.

The duration of this treatment depends upon the temperature of the bath. It may require about half a minute to one minute in said phospho-chromic solution, at between 50 to 100° C. It would require 5 minutes or more of treatment at about room temperature. For reasons which will be set forth hereinafter in connection with the operation described under 4, the preferred ranges of temperatures are 80° C. to 90° C. and a duration of half a minute to one minute will then give satisfactory results.

This operation leaves a dull surface on the pieces. The effect of this treatment is to render the aluminum surface uniform and to give a satin-like aspect on the entire surface whether the same has been previously polished or not. The solution acts as a cleaning agent and descaling agent for the aluminum, as it removes the alumina, but without any attack on the metal itself. The article is then preferably rinsed in running water.

3. The "brightening" of the surface, properly so-called, is the result of an anodic oxidation in an alkaline solution containing the ions phosphate PO_4^{---} and aluminate AlO_2^-. These ions are of course in combination with a metal, preferably an alkali metal such as sodium. The solutions accordingly can be economically prepared by dissolving trisodium phosphate and sodium aluminate in water. Also it could be prepared by dissolving aluminum phosphate in caustic soda solution or by any convenient means. In any case the PO_4^{---} ion in the solution, should be 2 to 20% and the AlO_2 ion should be 0.5% to 5%. The potassium compounds can be used instead of sodium compounds, if desired.

The pH of said alkaline phosphate aluminate solution should not be lower than about 11 and will be preferably near 12. In such highly alkaline solutions no aluminum phosphate can be formed as this compound is no more soluble and, in presence of the alkali metal, it gives the phosphate and the aluminate of said metal, e. g. with sodium Na_3PO_4 and $NaAlO_2$.

The piece to be brightened is made the anode in an electrolytic cell containing said solution.

The temperature of the solution can be between 70 and 95° C., according to the degree of brilliancy desired in the coating and the age of the bath. A bath which has been used for some time needs a temperature higher than a fresh bath. The anodic oxidation can be conducted at a tension of 8 to 20 volts, current intensity 4 to 10 amperes per square decimeter, time 5 to 10 minutes.

This anodic electrolytic treatment deposits a thin coating of aluminum hydroxide on the surface of the aluminum body, the aluminum of said coating coming from both the metal being treated and the aluminate ion in the solution.

The piece is then preferably rinsed, e. g. in running water. The phosphate-aluminate solution can be used until all of the alumina has been transformed into gelatinous condition when the bath will be discarded.

4. The preceding operations give a film of pulverulent aluminum hydroxide. This film is then dissolved and the uniformity of the brilliance of the surface is controlled, by means of a solution of phosphoric and chromic acid which may be the same as that described under 2 above. Or baths of similar compositions can be used. The article is immersed in the solution for 1 to 5 minutes, preferably about 3 minutes. The bath is at about 80 to 90° C. preferably between 83 to 87° C. and that is the reason why the same temperature is preferably used in the operation under 2 above, as it makes it possible to use the same bath for both Operations 2 and 4.

This solution leaves perfectly intact the brilliancy of brilliant parts and mat the others, rendering the solution a control means before the following operations in the course of which a coating of protective aluminum oxide, by anodic oxidation is formed. On the other hand it dissolves the clouds or veils which sometimes remain, in certain areas, from the brightening operation which are usually provoked by a difficulty caused by the disengagement of gas, particularly anodic oxygen.

The piece is then well rinsed in running water.

If, after this operation, there remains some dull areas on the surface of the aluminum article, Operations 3 and 4 can be repeated. If the surface of the aluminum or aluminum article is uniformly sufficiently reflective, the Step 5 (below) is then taken.

5. Anodic oxidation of the article in an acid solution. To this step, per se, no claim for novelty is made herein. The electrolyte can be a H_2SO_4 solution e. g. a 12% H_2SO_4 solution and the voltage may be for example 12 volts, the temperature being 18° C. to 22° C. Any anodic oxidation bath may be employed.

This operation has for its object to form on the surface of the article, a perfectly transparent coating of aluminum oxide, strongly adhering to the metal and sufficiently thick to preserve the brilliancy of the subadjacent bright aluminum, and which is resistant to atmospheric humidity.

The anodized article can then be subjected to a coloring treatment or the article can be subjected to a sealing treatment, e. g. in boiling water.

I prefer distilled water or water rid of its lime content. Dipping the article in boiling water for about ¼ hour will be sufficient. Other sealings may be employed, e. g. a sealing with an aqueous solution of nickel acetate at about 90° C.

As to the coloring treatment it may be said that the organic dyes are convenient. As an example, I can employ an aqueous solution of alizarin, at the temperature and the concentration corresponding to the colour to be obtained.

The invention can be illustrated and made readily understandable by the following examples, to the details of which the invention is not restricted.

Example 1

A plain aluminum plate is, after a preliminary polishing, degreased electrolytically in a solution of 5% sodium carbonate, 5% sodium phosphate and 2% sodium silicate at room temperature,

under a voltage of 10 to 12 volts, for about one minute, and then rinsed in water. It is then immersed in an aqueous solution containing 32% of phosphoric acid and 12% of chromic acid, e. g. in a lead or aluminum pan, and heated at about 85° C. The duration of this immersion can be one minute. The plate is removed and washed in running water.

It is then introduced as the anode, into a solution prepared by dissolving 100 grams NaOH in a liter of water, then dissolving therein 10 grams of powdered aluminum and adding 50 grams of phosphoric acid of 60° Bé. the cathode being two sheets of steel. The temperature of the bath is 80° C. The voltage applied is 12 volts, at 6 amperes per square decimeter, continued for 12 minutes. Take out the plate and rinse.

Then place it in the aforesaid bath of phosphochromic acid, i. e. 32% H_3PO_4 and 12% H_2CrO_4 at 85° C. for about 3 minutes. Remove plate and rinse in water.

Then submit the plate to anodic oxidation in a 12% H_2SO_4 solution, for 20 minutes, at a temperature of about 20° with a voltage applied of about 12 volts.

Rinse plate in water; then place plate in boiling water for 15 minutes, for "sealing." Take out and dry.

The aluminum plate has acquired a highly lustrous, brilliant, mirror-like surface having a reflecting power of 90 to 93% of that of silvered glass.

Example 2

A cast piece of alloy consisting of 95% Al, 4% Cu, 1% Mg, is polished and degreased as in Example 1. The first phospho-chromic acid solution can contain 30% H_3PO_4 and 15% H_2CrO_4, and is used at 83° C. Then rinse in water.

The piece is then introduced as the anode into a solution made by dissolving 100 grams NaOH in 1 liter of water and dissolved in this, 60 grams of aluminum phosphate, the cathode being the electrolytic cell itself. The temperature of the electrolytic bath is 95° C. The cell is operated at 10 volts, 8 amperes per square decimeter, for 5 minutes. The piece is taken out and rinsed.

It is immersed again for 2 minutes in the phospho-chromic acid solution described above. Take out and rinse.

Place again in the aforesaid alkaline aluminate-phosphate solution, as the anode, in the same operating conditions (95° C., 10 volts, 8 amp. per sq. dm.) and for 5 minutes. Then treat again for about 2 minutes in the phosphochromic acid solution. Take out and rinse.

Subject to anodic oxidation in the H_2SO_4 solution, color with a golden dye, and treat in boiling water for ten minutes. The piece will look like a jewelry article.

Example 3

A cast piece of alloy composed of 95% Al, 4% Cu, 1% Mg, is polished and degreased as in Example 1. The first phospho-chromic acid solution contains 35% H_3PO_4 and 10% H_2CrO_4 and is used at about 50° C. for one minute. Then rinse in water.

Introduce the piece as the anode into a solution made by dissolving 100 grams NaOH in 1 litre of water and dissolving in this 45 grams of aluminum phosphate. The temperature is 85° C. The cell is operated at 15 volts for 7 minutes. Then take out the piece and rinse.

Immerse it for 3 minutes in a phosphochromic solution made of 30% H_3PO_4 and 15% H_2CrO_4, the temperature being 85° C., remove and wash.

Place it again as the anode in the aluminate phosphate solution hereinabove described, under the same conditions, for 4 minutes, take out and rinse. Then submit the piece to anodic oxidation in a 3% oxalic acid solution, at room temperature, with an applied voltage of 30 volts during 30 minutes. Rinse and dip in boiling water for 10 minutes; take out and dry.

The cast piece is highly brightened, its reflection power being almost that of silvered glass.

The above specific examples are not intended as limitations, since it will be seen that many details can be varied. Many different compositions of the phosphochromic acid, and of the alkali phospho-aluminates can be used. The essentials of the invention include the three operations under 2, 3 and 4, with the phosphochromic acid serving to clean and descale, making mat surfaces, dissolving the coatings and pulverulent alumina, and controlling the extent of making the surface brilliant, all with the obligation that the solution in step 3 contains aluminate.

I claim:

1. The process of producing a permanently highly reflective surface on articles formed of aluminum and aluminum alloys comprising the steps of degreasing the article; washing the degreased article; immersing the article in a highly acid aqueous bath essentially consisting of 30% to 35% phosphoric acid and 10% to 15% chromic acid so as to clean the article by removing alumina therefrom without attacking the aluminum metal, thereby producing a satin-like surface on the washed article; electrolyzing the satin-like surfaced article in an aqueous alkaline bath consisting essentialy of an alkali metal phosphate and an alkali metal aluminate in an amount such that said bath contains between 2% to 10% phosphate ions and between 0.5% to 5% aluminate ions so as to produce a thin coating of aluminum hydroxide on a surface of the article, thereby brightening the same, the aluminum article being the anode in the electrolytic cell; washing the thus coated article; subjecting the thus coated and washed article to a highly acid aqueous bath essentially consisting of phosphoric acid and chromic acid so as to dissolve alumina on the surface of the article, thereby further and evenly brightening the coated surface of the aluminum article; and washing the thus treated article so as to recover the final permanently brightened aluminum article.

2. The process of producing a permanently highly reflective surface on articles formed of aluminum and aluminum alloys comprising the steps of degreasing the article; washing the degreased article; immersing the article in a highly acid aqueous bath essentially consisting of 30% to 35% phosphoric acid and 10% to 15% chromic acid at a temperature between 50° C. and 100° C. so as to clean the article by removing alumina therefrom without attacking the aluminum metal, thereby producing a satin-like surface on the washed article; electrolyzing the satin-like surfaced article in an aqueous alkaline bath consisting essentially of an alkali metal phosphate selected from the group consisting of sodium phosphate and potassium phosphate and an alkali metal aluminate selected from the group consisting of sodium aluminate and potassium aluminate in an amount such that said bath contains between 2% to 10% phosphate

and between 0.5% to 5% aluminate ions at a temperature between 70° C. and 95° C. so as to produce a thin coating of aluminum hydroxide on a surface of the article, thereby brightening the same, the aluminum article being the anode in the electrolytic cell; washing the thus coated article; subjecting the thus coated and washed article to a highly acid aqueous bath essentially consisting of phosphoric acid and chromic acid at a temperature between 80° C. and 90° C. so as to dissolve alumina on the surface of the article, and thereby further and evenly brightening the coated surface of the aluminum article; and washing the thus treated article so as to recover the final permanently brightened aluminum article.

3. The process of producing a permanently highly reflective surface on articles formed of aluminum and aluminum alloys comprising the steps of degreasing the article; washing the degreased article; immersing the article in a highly acid aqueous bath essentially consisting of 30% to 35% phosphoric acid and 10% to 15% chromic acid at a temperature between 80° C. and 90° C. so as to clean the article by removing alumina therefrom without attacking the aluminum metal, thereby producing a satin-like surface on the washed article; electrolyzing the satin-like surfaced article in an aqueous alkaline bath consisting essentially of an alkali metal phosphate selected from the group consisting of sodium phosphate and potassium phosphate and an alkali metal aluminate selected from the group consisting of sodium aluminate and potassium aluminate in an amount such that said bath contains between 2% and 10% phosphate ions and between 0.5% to 5% aluminate ions at a temperature between 70° C. and 95° C. so as to produce a thin coating of aluminum hydroxide on a surface of the article, thereby brightening the same, the aluminum article being the anode in the electrolytic cell; washing the thus coated article; subjecting the thus coated and washed article to a highly acid aqueous bath essentially consisting of phosphoric acid and chromic acid at a temperature between 83° C. and 87° C. so as to dissolve alumina on the surface of the article, thereby further and evenly brightening the coated surface of the aluminum article; and washing the thus treated article so as to recover the final permanently brightened aluminum article.

4. The process of producing a permanently highly reflective surface on articles formed of aluminum and aluminum alloys comprising the steps of degreasing the article; washing the degreased article; immersing the article in a highly acid aqueous bath essentially consisting of 30% to 35% phosphoric acid and 10% to 15% chromic acid at a temperature between 80° C. and 90° C. for one-half to one minute so as to clean the article by removing alumina therefrom without attacking the alumina metal, thereby producing

a satin-like surface on the washed article; electrolyzing the satin-like surfaced article in an aqueous alkaline bath consisting essentially of an alkali metal phosphate selected from the group consisting of sodium phosphate and potassium phosphate and an alkali metal aluminate selected from the group consisting of sodium aluminate and potassium aluminate in an amount such that said bath contains between 2% to 10% phosphate ions and between 0.5% to 5% aluminate ions at a temperature between 70° C. and 95° C. for five to ten minutes so as to produce a thin coating of aluminum hydroxide on a surface of the article, thereby brightening the same, the aluminum article being the anode in the electrolytic cell; washing the thus coated article; subjecting the thus coated and washed article to a highly acid aqueous bath essentially consisting of phosphoric acid and chromic acid at a temperature between 83° C. and 87° C. for one to five minutes so as to dissolve alumina on the surface of the article, thereby further and evenly brightening the coated surface of the aluminum article; and washing the thus treated article so as to recover the final permanently brightened aluminum article.

5. A process according to claim 1 in which the alkali metal phosphate is selected from the group consisting of sodium phosphate and potassium phosphate and the alkali metal aluminate is selected from the group consisting of sodium aluminate and potassium aluminate.

6. A process according to claim 1 in which the final permanently brightened aluminum article is subjected to anodic oxidation in an acid bath so as to form a transparent coating of alumina on the surface of the article, thereby preserving the brilliancy of the same.

7. A process according to claim 1 in which the pH of said aqueous alkaline bath is at least 11.

8. A process according to claim 1 in which the pH of said aqueous alkaline bath is about 12.

9. A process according to claim 4 in which the electrolyzing of the satin-like surfaced article in said aqueous alkaline bath is carried out at a voltage of 8–20 volts and a current intensity of 4–10 amperes per square decimeter.

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